

AD-A216 972

CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

| | | | |
|---|--|--|-------------------------|
| 1. RT SECURITY CLASSIFICATION | | 1b. RESTRICTIVE MARKINGS | |
| 2. RTY CLASSIFICATION AUTHORITY | | 3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited. | |
| 4. CLASSIFICATION/DOWNGRADING SCHEDULE Unclassified | | 5. MONITORING ORGANIZATION REPORT NUMBER(S) | |
| 6. FORMING ORGANIZATION REPORT NUMBER(S) N00014-79-C-0647 | | 7a. NAME OF MONITORING ORGANIZATION | |
| 7. NAME OF PERFORMING ORGANIZATION Colorado State University | 6b. OFFICE SYMBOL (If applicable) | 7b. ADDRESS (City, State, and ZIP Code) | |
| 8. ADDRESS (City, State, and ZIP Code) Department of Chemistry Fort Collins, CO 80523 | | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-79-C-0647 | |
| 8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research | 8b. OFFICE SYMBOL (If applicable) | 10. SOURCE OF FUNDING NUMBERS | |
| 8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000 | | PROGRAM ELEMENT NO. | PROJECT NO. |
| | | TASK NO. | WORK UNIT ACCESSION NO. |
| 11. TITLE (Include Security Classification) "Determination of the Minimum Energy Conformations of Benzyl Alcohol and 2-Phenethyl Alcohol" | | | |
| 12. PERSONAL AUTHOR(S) Hoong-Sun Im and E. R. Bernstein | | | |
| 13a. TYPE OF REPORT Technical Report | 13b. TIME COVERED FROM _____ TO _____ | 14. DATE OF REPORT (Year, Month, Day) December 14, 1989 | 15. PAGE COUNT |
| 16. SUPPLEMENTARY NOTATION | | | |
| 17. COSATI CODES | | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) | |
| FIELD | GROUP | SUB-GROUP | |
| | | supersonic jet mass spectroscopy, benzyl alcohol, 2-phenethyl alcohol, π -electron cloud, structure, conformation, internal hydrogen bonding | |
| 19. ABSTRACT (Continue on reverse if necessary and identify by block number) SEE ATTACHED ABSTRACT | | | |
| 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS | | 21. ABSTRACT SECURITY CLASSIFICATION Unclassified | |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL Elliot R. Bernstein | | 22b. TELEPHONE (Include Area Code) (303) 491-6347 | 22c. OFFICE SYMBOL |

DTIC
ELECTE
JAN 25 1990
S B D

90 01 24 0 25

OFFICE OF NAVAL RESEARCH

Contract N00014-79-C-0647

TECHNICAL REPORT #63

"Determination of the Minimum Energy Conformations of Benzyl
Alcohol and 2-Phenethyl Alcohol"

by

Hoong-Sun Im and E. R. Bernstein

Submitted for publication

Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

December 14, 1989

Reproduction in whole or in part is permitted for
any purpose of the United States Government.

This document has been approved for public release
and sale; its distribution is unlimited

Determination of the Minimum Energy

Conformations of Benzyl Alcohol

and 2-Phenethyl Alcohol

Hoong-Sun Im and E.R. Bernstein

Department of Chemistry
Colorado State university
Fort Collins, Colorado 80523

and

Jeffery I. Seeman

The Philip Morris Research Center
P.O. Box 26583, Richmond, Virginia 23261

Abstract

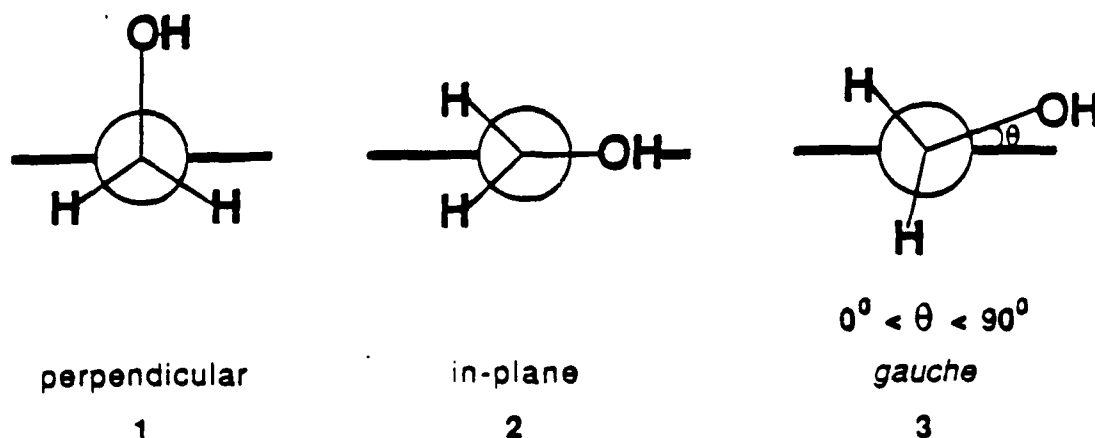
Supersonic jet mass resolved excitation spectroscopy is employed to determine the minimum energy conformation of the alcohol group with respect to the benzene ring for benzyl alcohol (BA) and 2-phenethyl alcohol (2-PEA). The mass resolved excitation spectra of these molecules are presented and assigned. The C-O bond orientation in BA is determined to be perpendicular to the benzene ring ($\tau(\text{Cortho-Cipso-C}\alpha\text{-O}) = 90^\circ$) and in 2-PEA it is determined to be gauche with respect to the $\text{Cipso-C}\alpha$ bond ($\tau(\text{Cipso-C}\alpha\text{-C}\beta\text{-O}) = \pm 60^\circ$). By considering the OH \cdots π -electron cloud internal hydrogen bonding and the repulsive interaction between the non-bonding electrons on the oxygen atom and π -electron cloud, the hydroxyl proton in both molecules is suggested to be pointing toward the benzene ring.

| | |
|--------------------|-------------------------------------|
| Accession For | |
| NTIS GRA&I | <input checked="" type="checkbox"/> |
| DTIC TAB | <input type="checkbox"/> |
| Unannounced | <input type="checkbox"/> |
| Justification | |
| By | |
| Distribution/ | |
| Availability Codes | |
| Dist | Avail and/or Special |
| A-1 | |

I. Introduction

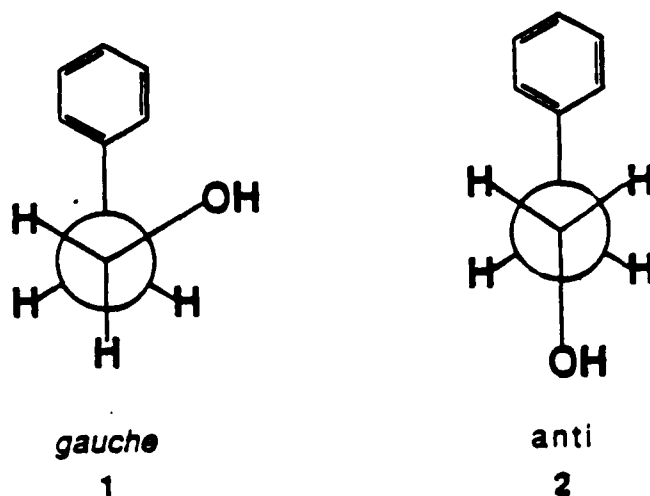
A variety of conformations are possible for benzyl alcohol (BA) and 2-phenethyl alcohol (2-PEA) considering the orientations of the C-O and O-H bonds. If only the C-O bond orientation is considered, as shown in Scheme I, three distinct conformers are available to BA: C-O bond perpendicular to the plane of the aromatic ring (I-1); C-O bond in the plane of the aromatic ring (I-2); and C-O bond at some angle, $0^\circ < \theta < 90^\circ$, with respect to the plane of the ring (I-3).

Scheme I



Two C-O bond conformers exist for 2-PEA, as shown in scheme II: the gauche conformer (II-1) and the anti conformer (II-2).

Scheme II



Each one of these C-O bond conformers for BA and 2-PEA may evidence different conformations for the hydrogen atom of the hydroxyl group.

The stable conformations of BA and 2-PEA have been investigated by several different spectroscopic and theoretical approaches. These efforts have attempted to elucidate the oxygen atom position as described above and the possibility of intramolecular hydrogen bonding between the hydroxyl hydrogen and the aromatic π -electron cloud.

Based on the observation of two OH stretching vibrations in the IR spectra¹, two stable conformations are suggested to exist for both alcohols in dilute solution - a non-hydrogen bonded conformer in which the hydroxyl hydrogen atom points away the aromatic ring and a hydrogen bonded conformer in which the hydroxyl hydrogen atom coordinates to the aromatic ring. The hydrogen bonded conformer is suggested to be the predominant one for the two aryl alcohols in solution. These studies are not able to draw any conclusions concerning the position of the oxygen atom in BA, however. Nonetheless, for 2-PEA, the gauche C-O bond orientation (II-1) is proposed for the hydrogen bonded conformer and the anti C-O bond orientation (II-2) is proposed for the non-hydrogen bonded conformers.

The several NMR studies for BA which have been reported are not able to reach a consensus on which conformer is most stable with respect to the position of oxygen: both the in-plane conformation (I-2)² and the gauche conformation (I-3, $\theta = -60^\circ$)³ are suggested to be the most stable structure. Moreover, ab initio (STO-3G) and molecular mechanics calculations for BA do not agree on the orientation of the hydroxyl proton: molecular mechanics calculations obtain the in-plane hydrogen bonded conformer as most stable⁴, while the STO-3G calculation predicts the in-plane non-hydrogen bonded conformer as most stable.⁵ For 2-PEA, NMR studies, IR studies and

5

molecular mechanics calculations (MMPMI) reach the same conclusion: the hydrogen bonded gauche conformer (II-1) is more stable than the anti conformer (II-2) by 1.2 kcal/mol.⁶

Recent electron diffraction studies of gaseous BA suggest the oxygen atom is out of the plane of the aromatic ring by 54° (I-3, $\theta = 54^\circ$) and that the hydroxyl hydrogen coordinates to the ring.⁷ No comparable electron diffraction data are available for 2-PEA.

In summary, the orientation of the alcohol group in isolated molecules of these two aryl alcohols remains an open and unsettled issue.

In the present study, laser supersonic jet spectroscopy is employed to identify the geometry of the stable conformation(s) of BA and 2-PEA. Since each stable conformation of a molecule has a specific potential energy minimum in the ground state, the energy of the electronic origin for the $S_1 \leftarrow S_0$ transition for each stable conformer is usually unique. In other words, each stable conformer generates its own origin transition. Thus, the number of origins that occur in the absorption spectrum of a molecule corresponds to the number of stable conformations of that molecule.

We present the absorption spectra of BA, 2-PEA and their derivatives detected by time-of-flight mass spectroscopy (TOFMS - mass resolved excitation spectroscopy). By comparing the number of origins in the spectra of various substituted BA's and 2-PEA's to those predicted by the symmetry of each conformation (Scheme I and Scheme II), orientations of the C-O bonds in these alcohols can be determined. These data also lead to conclusions concerning the orientations of the O-H bonds in BA and 2-PEA. The possibilities of OH \cdots π -electron cloud internal hydrogen bonding, and the interaction between the aromatic π -cloud and the lone-pair electrons on the oxygen atom will be discussed for these systems.

II. Experimental Procedures

A pulsed supersonic molecular beam is generated using an R.M. Jordan pulsed valve. All the samples are placed inside the valve head and heated to about 500 C to increase their concentration in the beam. Ar or He is used as the carrier gas with a ~ 4 atm backing pressure. All the spectra are obtained using one-color, two-photon resonance enhanced ionization with TOFMS detection (mass resolved excitation spectra). The TOFMS chamber is as described elsewhere.⁸ A Nd³⁺/YAG laser is used to pump a dye laser-doubling/mixing system. The doubled output of LDS 698 mixed with the residual 1.064 μm Nd³⁺/YAG beam is employed to provide both the pump and ionization photons.

BA, 3-fluorobenzyl alcohol (3-FBA), 4-ethylbenzyl alcohol (4-EtBA), 2-methylbenzyl alcohol (2-MeBA), 3-methylbenzyl alcohol (3-MeBA), 2-PEA, 2-(*o*-methyl phenyl)-ethanol (2-(*o*-CH₃)-PEA) and 2-(*m*-methyl-d₃-phenyl)-ethanol (2-(*m*-CH₃)-PEA) are obtained from Aldrich. The samples of partially deuterated benzyl alcohols (BA-d₂, C₆H₅CD₂OH) and 2-(*m*-methyl-d₃-phenyl)-ethanol (2-(*m*-CD₃)-PEA) are synthesized as described in the supplementary material for this paper. All samples are studied as received and not further purified.

III. Results

A. Benzyl alcohol and its derivatives

1. Benzyl alcohol and Benzyl alcohol-d₂

Fig. 1(a) shows the TOFMS of jet-cooled benzyl alcohol around the origin region of the $S_1 \leftarrow S_0$ transition. In this spectrum, four distinct features are found at 37526.6 (A), 37577.2 (B), 37623.5 (c), and 37649.1 (D) cm^{-1} . The assignment of the four peaks in this spectrum is not clear: that is,

does the spectrum consist of one origin and its vibronic features, or are several origins present (suggesting several conformations of BA)? In order to address this question, the spectrum of BA-d₂ is studied.

One expects that the BA and BA-d₂ isotopes should have the same conformational energy and O_0^0 transitions and thus little or no isotope effect would be observed for the features associated with $S_1 \leftarrow S_0$ origin transitions of the stable conformers. On the other hand, vibronic features of BA-d₂ will show an isotope shift with respect to those of BA.

The TOFMS spectrum of BA-d₂ in the O_0^0 region is shown in Fig. 1(b). As seen in Fig. 1, even though the total mass change is small (108 amu to 110 amu, 1.8%), the isotopic shift of each feature from the first peak in the BA-d₂ spectrum is substantial. The isotope shift ranges from 3% to 8% for these features. These isotope effect data for each feature are collected in Table I. The data suggest that the first peak in each spectrum is an origin (37526.6 and 37543.8 cm⁻¹ for BA and BA-d₂, respectively), that the second and the third peaks belong to a progression in one vibration, and that the fourth peak arises from another vibrational mode. Because of the relative change of frequency with isotopic substitution, the 2nd and 3rd peaks are assigned to the progression of the torsional vibration of the -CH₂OH group. Even though the isotope effect of the 4th peak is relatively small, it is not likely an origin because no vibronic progression can be identified following it. This later peak is assigned as the fundamental of a molecular vibration (see Table I).

2. 4-Ethylbenzyl alcohol

The spectrum of 4-EtBA is depicted in Fig. 2. It displays two origins at 36992.0 and 36999.5 cm⁻¹, respectively. The same vibronic features (B, C, D)

found in the spectrum of BA also appear to be built on both of these origins. The data are collected in Table II. Since two origins are observed, this molecule has two stable conformers in the ground state.

3. 3-Methylbenzyl alcohol and 3-Fluorobenzyl alcohol

The TOFMS of jet-cooled 3-MeBA is presented in Fig. 3. As found for meta substituted toluenes⁹, the origin is composed of a doublet due to the methyl torsion: the several doublets to the blue of the origin doublet at 36944.7 and 36945.8 cm^{-1} are assigned as due to the $-\text{CH}_2\text{OH}$ torsional motion upon which is superimposed the methyl torsion. The symmetry of BA is lowered by the meta methyl substitution and thus the fundamental of the torsional vibration of the $-\text{CH}_2\text{OH}$ group becomes spectroscopically allowed. This torsional motion in BA and its derivatives will be discussed in more detail in a later paper. The above results thus confirm the interpretation that only one stable conformer exists for BA. Further discussion will be presented concerning these doublet structures and their interpretation below. The spectroscopic data are collected and assigned in Table III.

The TOFMS of 3-FBA is displayed in Fig. 4. This spectrum is very similar to that of BA; one origin at 37331.6 cm^{-1} , a torsional progression built on it, and one totally symmetric fundamental (ν_{16b}) (see Table IV). The assignments of these peaks are thus exactly the same as those for BA. This molecule has a single stable conformer, just as BA.

4. 2-Methylbenzyl alcohol

The mass resolved excitation spectrum of 2-MeBA detected by TOFMS is shown in Fig. 5. Only one strong origin is present in the spectrum at

37134.1 cm^{-1} . Because of the steric hindrance between the substituents, no torsional progression is observed. This result implies that 2-MeBA has only one stable conformer.

B. 2-Phenethyl alcohol and its derivatives

1. 2-Phenethyl alcohol

The TOFMS of jet-cooled 2-PEA is displayed in Fig. 6. The spectrum presents only one intense origin feature at 37622.2 cm^{-1} , corresponding to one stable conformer of the molecule. The remaining weak features to higher energy of the origin in Fig. 6 are assigned as due to motions of the ethanol chain. These weak features are similar to the features observed in the TOFMS of the ethylbenzenes.^{9b}

2. 2-(*m*-Methylphenyl)-ethanol and 2-(*m*-Methyl- d_3 -phenyl)-ethanol

The TOFMS of 2-(*m*- CH_3)-PEA, presented in Fig. 7, shows an intense origin which appears as a multiple of at least three features. A higher resolution scan of this origin (shown in the upper part of Fig. 7) reveals that this transition is composed of 4 distinct features (37081.0, 37804.1, 37085.4 and 37088.0 cm^{-1}). Based on the experimental data for other meta-substituted toluenes, one expects that the origin(s) of 2-(*m*- CH_3)-PEA will show doublet structure(s) due to methyl torsion transitions.⁹ From this point of view, the quartet structure of the origin must arise from two stable conformers of this molecule: the first two peaks belong to the origin of one conformer and the last two peaks belong to that of the other. Notice that the separation of two origin transitions is ca. 4 cm^{-1} .

The mass resolved excitation spectrum of jet-cooled 2-(*m*- CD_3)-PEA is displayed in Fig. 8. The 0_0^0 transition of this isotopic species is a clear

doublet: the substitution of CD_3 for CH_3 has reduced the interference from methyl rotor transitions and thus the origin features due only to the conformational difference can be clearly observed. Two origins are observed for 2-(*m*- CD_3)-PEA at 37105.9 and 37109.0 cm^{-1} .

3. 2-(*o*-Methylphenyl)-ethanol

The absorption spectrum of 2-(*o*- CH_3)-PEA detected by TOFMS (Fig. 9) shows only one strong origin at 37212.6 cm^{-1} . Because of the large steric hindrance between the methyl and ethanol ring substituents, only one conformer can exist as a stable form of the molecule.

VI. DISCUSSION

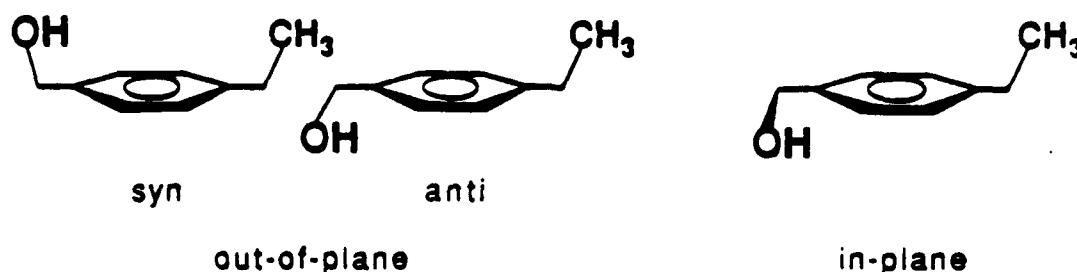
A. Determination of the C-O bond orientation

1. Benzyl alcohol

Only one origin is observed for BA and BA- d_2 , and thus only one stable conformation exists for BA. In the stable conformer, the C-O bond orientation should be one of those shown in scheme I: perpendicular (I-1), planar (I-2), or gauche (I-3).

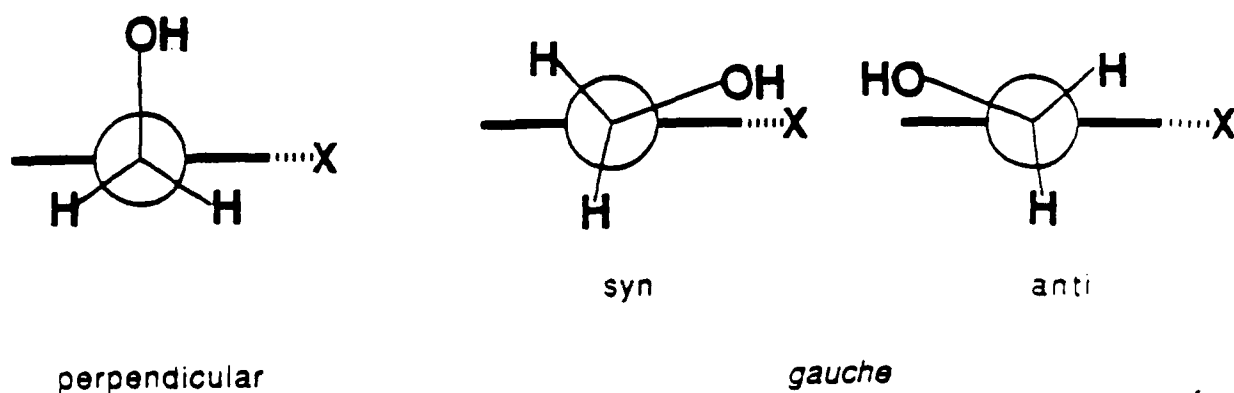
Since the CH_3 moiety in the ethyl group of ethylbenzene is known to be perpendicular to the plane of the ring,^{9b} the presence of the ethyl group at the para position of BA will result in two stable conformations if the C-O bond has an out-of-plane orientation and in one stable conformation if the C-O bond has an in-plane orientation. The possible conformers of 4-EtBA are shown in Scheme III.

Scheme III



4-EtBA displays two origins (see Fig. 2): the C-O bond is thus out of the aromatic ring plane. The C-O bond orientation is then either perpendicular or gauche. The two choices can be distinguished by examining meta-substituted BAs. The presence of a substituent (CH_3 , CD_3 , or F) at the meta position of BA will result in one conformer for the perpendicular C-O bond orientation, but in two conformers for the gauche C-O bond orientation (see Scheme IV).

Scheme IV



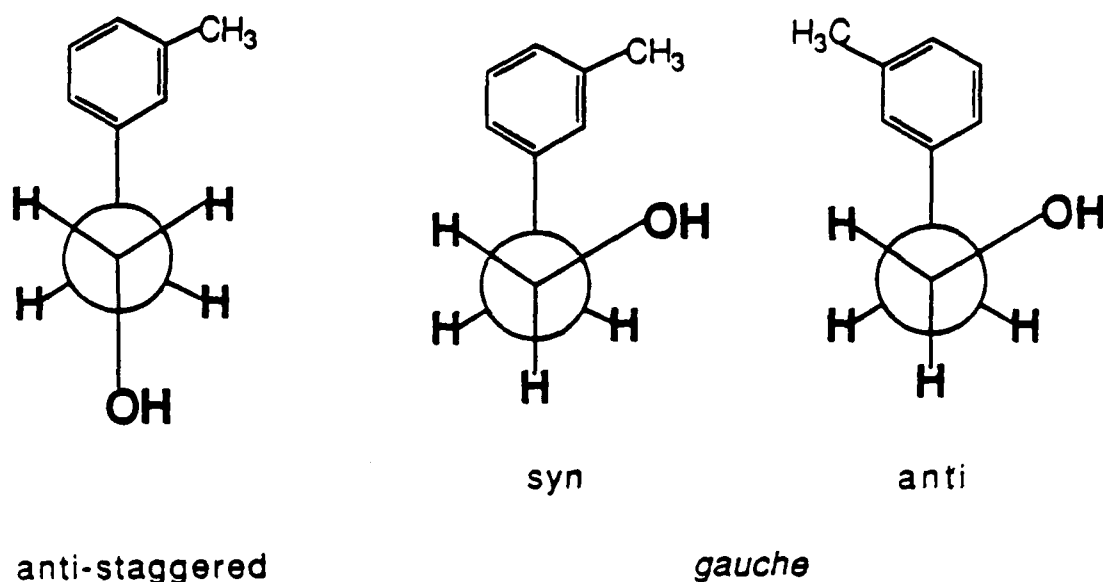
3-MeBA and 3-FBA are chosen for this later determination. The TOFMS of these molecules display only one origin (see Fig. 3 and 4): only one stable conformer exists for 3-MeBA and 3-FBA. The C-O bond is thus perpendicular to the plane of the ring in the stable conformer.

BA has a perpendicular basic heavy atom geometry while methoxy benzene¹⁰ and phenol¹¹ have a planar heavy atom geometry. Apparently, the oxygen lone-pair electrons can stabilize a planar conformation if the oxygen is attached directly to the ring but not if the oxygen atom is one carbon atom removed from the ring.¹²

2. 2-Phenethyl alcohol

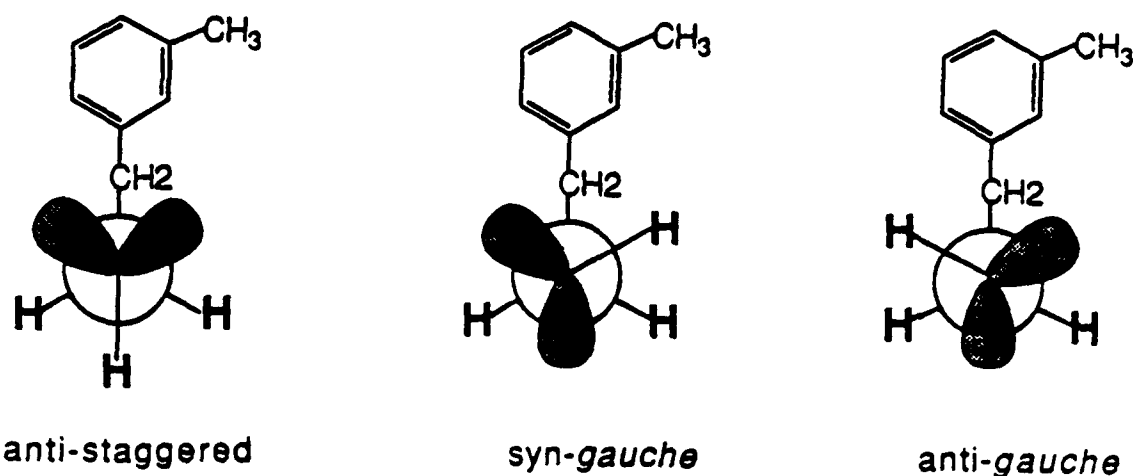
The mass resolved excitation spectrum of 2-PEA has only one origin. We conclude that only one stable conformer exists for this molecule: anti-staggered (II-1) or gauche (II-2). In order to determine which one of these is the more stable, 2-(m-CH₃)-PEA is chosen for study. The presence of the substituent at the meta position of 2-PEA will result in one origin for the anti-staggered conformer, but in two origins for the gauche conformer (see Scheme V).

Scheme V



From the spectra of 2-(m-CH₃)-PEA and 2-(m-CD₃)-PEA, we can conclude that 2-(m-methylphenyl)-ethanol has two origins separated by ~ 4 cm⁻¹; however, the assignment of those two origins to conformer structures is not clear because the energy difference between them is so small. Note that the syn- and anti- gauche conformers of m-n-propyltoluene are separated by ~ 60 cm⁻¹.^{9a} One can suggest that the ~ 4 cm⁻¹ splitting in 2-(m-CH₃)-PEA could also be due to the rotational isomers of the OH group, as shown in Scheme VI.

Scheme VI



Since these latter OH rotamers would have very small interaction with the methyl group at the meta position of 2-(m-CH₃)-PEA, the origins for two gauche conformers could have the same energy. The choice of either the anti- and syn-gauche C-O bond conformers (Scheme V) or the anti and gauche O-H bond rotamers (Scheme VI) as the cause for this 4 cm⁻¹ splitting can be made by the investigation of the spectra of 2-(o-CH₃)-PEA. The O-H rotamers of 2-(o-CH₃)-PEA will generate a larger origin doublet separation than those of 2-(m-CH₃)-PEA because the interaction between the hydroxyl hydrogen and the methyl group is larger for 2-(o-CH₃)-PEA than for 2-(m-CH₃)-PEA. On the other hand, for the C-O bond conformer, the syn-gauche conformer will be reduced in population due to severe steric hindrance between two ring substituents. Only an anti-gauche C-O bond conformer will thus yield one origin for 2-(o-CH₃)-PEA molecule. Since only one origin is observed in the spectrum of this molecule (see Fig. 9), we conclude that the gauche conformer of the C-O bond (II-1) is more stable for the 2-PEA molecule.

B. Determination of the O-H bond orientation

1. Benzyl alcohol

The doublet origin in 3-MeBA could be interpreted as due to the rotational isomer of the hydroxy group, or methyl torsion transitions. In order to resolve this question, 3-FBA is chosen and examined by TOFMS. Separation of the two O-H rotamer ^{10}S transitions for 3-fluorophenol^{11a} is $\sim 210\text{ cm}^{-1}$ vs $\sim 110\text{ cm}^{-1}$ for 3-methylphenol¹²; this separation is $\sim 140\text{ cm}^{-1}$ for 3-fluoroanisole¹⁴ vs $\sim 60\text{ cm}^{-1}$ for 3-methylanisole.^{10a} One can expect therefore that in 3-FBA the separation of the two O-H rotamer origins will be much larger than that found for 3-MeBA (1 cm^{-1} , see Table III) if the two origin features are due to OH rotational isomers. The observation of only one origin in the TOFMS of 3-FBA, however, excludes the possibility of the OH rotational isomer. This origin structure for 3-MeBA must be caused by methyl rotor torsional motion. The above results lead one to suggest that the hydroxyl hydrogen is symmetric (either anti or eclipsed) with respect to the aromatic ring. This conclusion is further supported by the investigation of 2-MeBA: in the mass resolved excitation-spectrum of this molecule, only one origin (see Fig. 5) is observed.

The rotational barrier for the OH group in ethanol is known to be $\sim 350\text{ cm}^{-1}$ ¹⁵; this barrier in BA is almost certainly higher than 350 cm^{-1} and thus the hydrogen atom is in a fixed position. The results of a MOPAC (5.0) molecular mechanics calculations using an AM1 hamiltonian also agree with the above expectation. The rotational barrier is calculated to be $\sim 500\text{ cm}^{-1}$. Nonetheless, whether the hydrogen is in the anti or eclipsed position cannot be determined from these experiments. Based on the hydrogen bonding considerations and a presumed repulsion between lone-pair electrons on the oxygen atom and the aromatic π -electrons, we suggest

that the hydroxyl hydrogen is locked over the aromatic ring in the eclipsed conformation.

2. 2-Phenethyl alcohol

From the results of the C-O orientation study for 2-PEA, we conclude that the gauche conformation of the C-O bond (Scheme II-1) yields the more stable molecular geometry even though this conformation is much more crowded than the anti-staggered conformation. The hydrogen bonding interaction, which is available to this structure, therefore must overcome the steric hindrance of this gauche conformation. In order to establish the intramolecular hydrogen bonding interaction, the hydrogen of the OH group must be pointing toward the ring and must be in a fixed conformation.

V. Summary and Conclusion

Supersonic jet mass resolved excitation spectroscopy techniques are capable of resolving the origins of individual stable conformations of molecules such as substituted BAs and 2-PEAs. Comparing the number of origins observed in the excitation spectrum to that expected by symmetry arguments, we have been able to determine the most stable conformations of these two isolated aryl alcohols.

In the most stable conformation of BA, the C_{α} -O bond is perpendicular to the aromatic ring plane and the hydroxyl hydrogen points toward the ring in an eclipsed position. The most stable conformation of 2-PEA has a gauche conformation of the C_{β} -O bond with respect to the C_{α} - C_{β} bond, and the hydrogen atom in the OH group points toward the phenyl ring (see Fig. 10).

These stable conformations of both isolated molecules suggest that intramolecular hydrogen bonding occurs between the OH hydrogen and

π -electrons of the phenyl ring. This hydrogen bonding overcomes the steric strain which exists in the stable conformations (see Fig. 10). In 2-PEA, this hydrogen bonding effect is important for the formation of the stable conformation. The interactions between the lone-pair electrons on the oxygen atom and the π -electrons must be somewhat repulsive in these aryl alcohols, unlike those found for phenol or anisole.

ACKNOWLEDGMENT

We wish to thank A.C. Lilly, B. LaRoy, R. Ferguson and J. Whidby for encouragement in and support of this effort. This work was supported in part by ONR.

References

1. (a) D.I. Campbell, G. Eglinton and R.A. Raphael, *J. Chem Soc. B*, 338 (1968).
(b) A.E. Lutskii, V.A. Granzhan, Y.A. Shuster and P.M. Zaitsev, *Zh. Prikl. Spektrosk* 11, 913 (1969).
(c) V.A. Granzhan, Y.A. Shuster, N.A. Barba, K.F. Kentenaru, L.S. Chasovskikh and S.F. Mandy, *Zh. Prikl. Spektrosk.* 20, 473 (1974).
(d) P. von R. Schleyer, C. Winter, D.S. Trifan and R. Bacskai, *Tetrahedron Lett.* 14, 1 (1959).
(e) H. Iwamura, *Tetrahedron Lett.* 26, 2227 (1970).
2. R.J. Abraham and J.M. Bakke, *Tetrahedron* 34, 2947 (1978).
3. T. Schaeffer, W. Danchura, W. Niemczura and W.J.E. Parr, *Can. J. Chem.* 56, 1721 (1978).
4. W.J. Hehre, L. Radom and J.A. Pople, *J. Am. Chem. Soc.* 94, 1496 (1971).
5. P. Loftus, Ph.D. Thesis, University of Liverpool (1971).
6. (a) S.L. Spassov, M.F. Simeonov, and E.W. Randall, *J. Mol. Struct.* 77, 289 (1981).
(b) J.M. Bakke, *Acta Chem. Scand.* B40, 407 (1986).
(c) J.M. Bakke and D.J. Chadwick, *Acta Chem. Scand. Ser. B*42, 223 (1988).
7. M. Traetteberg, H. Oestensen and R. Seip, *Acta Chem. Scand.* A34, 449 (1980).
8. E.R. Bernstein, K. Law, and M. Schauer, *J. Chem. Phys.* 80, 207 (1984).

9. (a) P.J. Breen, J.A. Warren, E.R. Bernstein, and J.I. Seeman, *J. Chem. Phys.* 87, 1927 (1987).
(b) P.J. Breen, E.R. Bernstein, and J.I. Seeman, *J. Chem. Phys.* 87, 3269, (1987).
10. (a) P.J. Breen, E.R. Bernstein, H.V. Secor and J.I. Seeman, *J. Am. Chem. Soc.* 111, 00000, (1989)
(b) A. Oikawa, H. Abe, N. Mikami, and M. Ito, *Chem. Phys. Lett.* 116, 50 (1985).
11. (a) A. Oikawa, H. Abe, N. Mikami, and M. Ito, *J. Phys. Chem.* 88, 5180 (1984).
(b) T.M. Dunn, R. Tembreull, and D.M. Lubman, *Chem. Phys. Lett.* 121, 453 (1985).
12. R.J. Abraham and J.M. Bakke, *Acta. Chem. Scand. B* 37, 865 (1983).
13. H. Mizuno, K. Okuyama, T. Ebata, and M. Ito, *J. Phys. Chem.* 91, 5589 (1987).
14. Hoong-Sun Im and E.R. Bernstein (unpublished results).
15. A.E. Dorigo, D.W. Pratt, and K.N. Houk, *J. Am. Chem. Soc.* 109, 6591 (1987).

Figure Captions

- Figure 1. TOFMS of jet-cooled BA (a) and BA-d₂ (b) around their 0_0^0 regions. Both molecules show only one origin (indicated as A) at 37526.6 and 37543.8 cm⁻¹ for BA and BA-d₂, respectively. See Table I for the assignments of the other features (B, C, D).
- Figure 2. TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ for jet-cooled 4-EtBA. The spectrum contains two origins at 36992.0 (syn conformer) and 36999.5 cm⁻¹ (anti conformer). The vibronic features belonging to each origin are bracketed and labeled. See Table II for the assignment of the vibronic features indicated.
- Figure 3. TOFMS of jet-cooled 3-MeBA around its 0_0^0 region. Only one origin is evident in this spectrum at 36945.8 cm⁻¹. The origin appears as doublet due to transitions between internal rotational states of the ring methyl group. See Table III for vibronic assignments.
- Figure 4. TOFMS of 3-FBA around its 0_0^0 region. The spectrum looks almost the same as that of BA: one origin at 37331.6 cm⁻¹, a torsional progression built on it, and one totally symmetric fundamental. See Table IV for vibronic assignments.
- Figure 5. TOFMS of the 0_0^0 region of $S_1 \leftarrow S_0$ for jet-cooled 2-MeBA. The spectrum shows a single intense origin at 37138.1 cm⁻¹.
- Figure 6. TOFMS of the 0_0^0 region of $S_1 \leftarrow S_0$ for jet-cooled 2-PEA. The single intense feature is assigned as the origin and occurs at 37622.2 cm⁻¹. The weak features to higher energy of the origin are presumed to be due to torsional motion of the ethanol group. The solitary origin demonstrates that only one stable conformer exists for this molecule.
- Figure 7. TOFMS of jet-cooled 2-(m-CH₃)-PEA around its origin region. The inset spectrum taken at higher resolution reveals the 0_0^0 to be a quartet. Considering the doublet appearance at the origins of m-substituted toluenes, the two origins due to conformational differences are assigned at 37084.1 and 37088.0 cm⁻¹.

Figure 8 TOFMS of the 0_0^0 region of $S_1 \leftarrow S_0$ for jet-cooled 2-(m-CD₃)-PEA. The substitution of CD₃ for CH₃ has reduced the rotational constant of the methyl torsion by a half and thus only the two origins due to conformational differences are observed (37105.9 and 37109.0 cm⁻¹).

Figure 9 TOFMS of the 0_0^0 region of $S_1 \leftarrow S_0$ for jet-cooled 2-(o-CH₃)-PEA. The spectrum presents only one intense feature at 37212.6 cm⁻¹, which is assigned as origin. In this molecule, only one stable conformer can exist because of the high steric hindrance between the two ring substituents (see text).

Figure 10 The geometry of the minimum energy conformers for BA(a) and 2-PEA(b). The stable conformer of BA is determined to have $\tau(\text{Cortho-Cipso-C}\alpha\text{-O}) = 90^\circ$ (i.e. the OH group is perpendicular to the benzene ring) and $\tau(\text{Cipso-C}\alpha\text{-O-H}) = 0^\circ$ (i.e., the hydroxyl proton is pointing toward the ring with the eclipsed orientation), and that of 2-PEA is determined to have $\tau(\text{Cipso-C}\alpha\text{-C}\beta\text{-O}) = \pm 60^\circ$ (i.e., the C β -O bond is gauche with respect to the Cipso-C α bond) and $\tau(\text{C}\alpha\text{-C}\beta\text{-O-H}) = \pm 60^\circ$ (i.e., the hydroxyl hydrogen is pointing toward the ring). The OH ... π internal hydrogen bonding occurs in both molecules.

TABLE I

Positions and assignments for BA and BA-d₂ features in the 0_0^0 region of ($S_1 \leftarrow S_0$).

| ν_a | BA $\nu-\nu(0_0^0)$ (cm ⁻¹) | BA-d ₂ $\nu-\nu(0_0^0)$ (cm ⁻¹) | isotope shift | Assignment |
|---------|--|---|---------------|------------|
| A | 0(37526.6) | 0(37543.8) | - | 0_0^0 |
| B | 50.6 | 46.7 | 8% | T_0^2 |
| C | 96.9 | 89.1 | 8% | T_0^1 |
| D | 122.5 | 118.9 | 3% | $16b_0^1$ |

a. A through D are the notation for the observed vibronic features in each molecule (see Fig. 1).

TABLE II

Positions and assignments for features of each conformer of 4-EtBA in the O_0^0 region of ($S_1 \leftarrow S_0$).

| ν^a | syn conformer ^b $\nu-\nu(O_0^0)(\text{cm}^{-1})$ | anti conformer ^b $\nu-\nu(O_0^0)(\text{cm}^{-1})$ | Assignment |
|---------|--|---|------------|
| A | 0 (36992.0) | 0 (36999.5) | O_0^0 |
| B | 47.2 | 46.4 | T_0^2 |
| C | 93.9 | 91.2 | T_0^1 |
| D | 119.4 | 121.3 | $16b_0^1$ |

- a. A through D are the notation for the observed vibronic features belonging to each conformer (see Figs. 1 and 2).
- b. The assignment for the specific conformation is based on the experimental results of diethylbenzene.^{9b}

TABLE III

Positions and assignments for features of 3-MeBA in the O_0^0 region of ($S_1 \leftarrow S_0$).

| ν^a | I($1e \rightarrow 1e$) ^b $\nu-\nu(O_0^0)(\text{cm}^{-1})$ | II($0a_1 \rightarrow 0a_1$) ^b $\nu-\nu(O_0^0)(\text{cm}^{-1})$ | Assignment |
|---------|---|--|------------|
| A | 0 (36944.1) | 0 (36945.8) | O_0^0 |
| B | 23.1 | 24.7 | T_0^1 |
| C | 47.1 | 49.1 | T_0^2 |
| D | 128.2 | 129.1 | $16b_0^1$ |

a. A through D are the notation for the observed vibronic features in Fig. 3.

b. The assignment for the transition is based on the experimental results of meta substituted toluenes.^{9a}

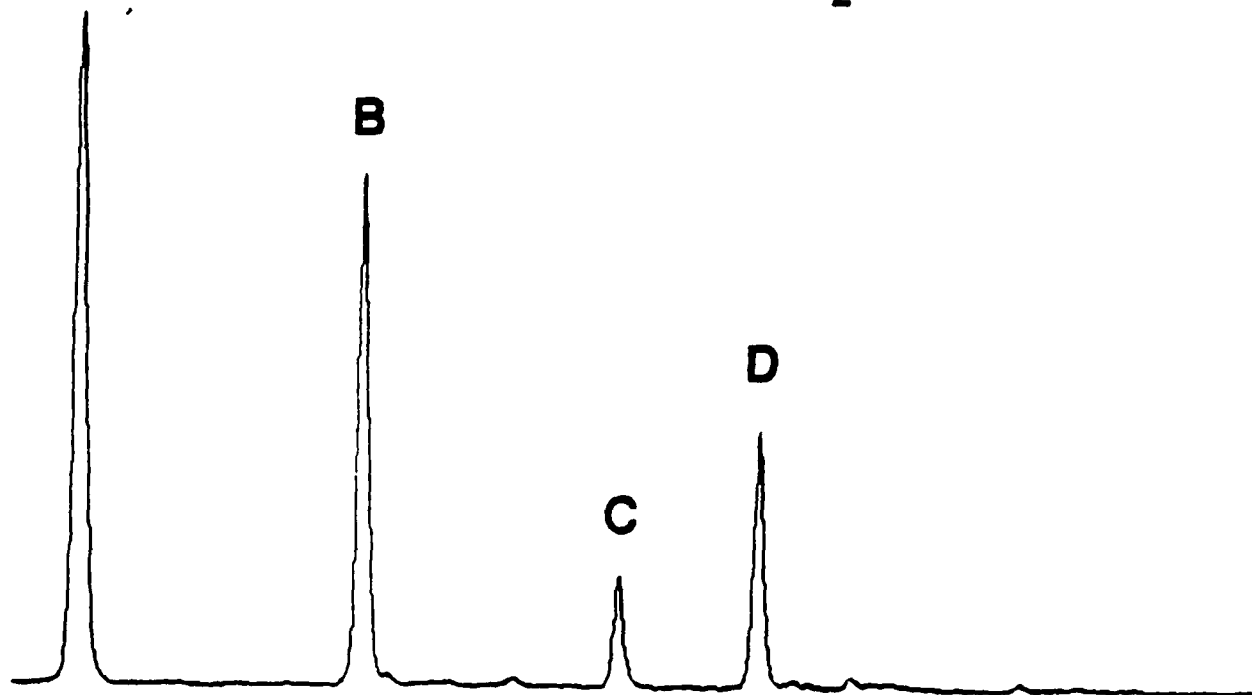
TABLE IV

Positions and assignments for features of 3-FBA in the 0_0^0 region of ($S_1 \leftarrow S_0$).

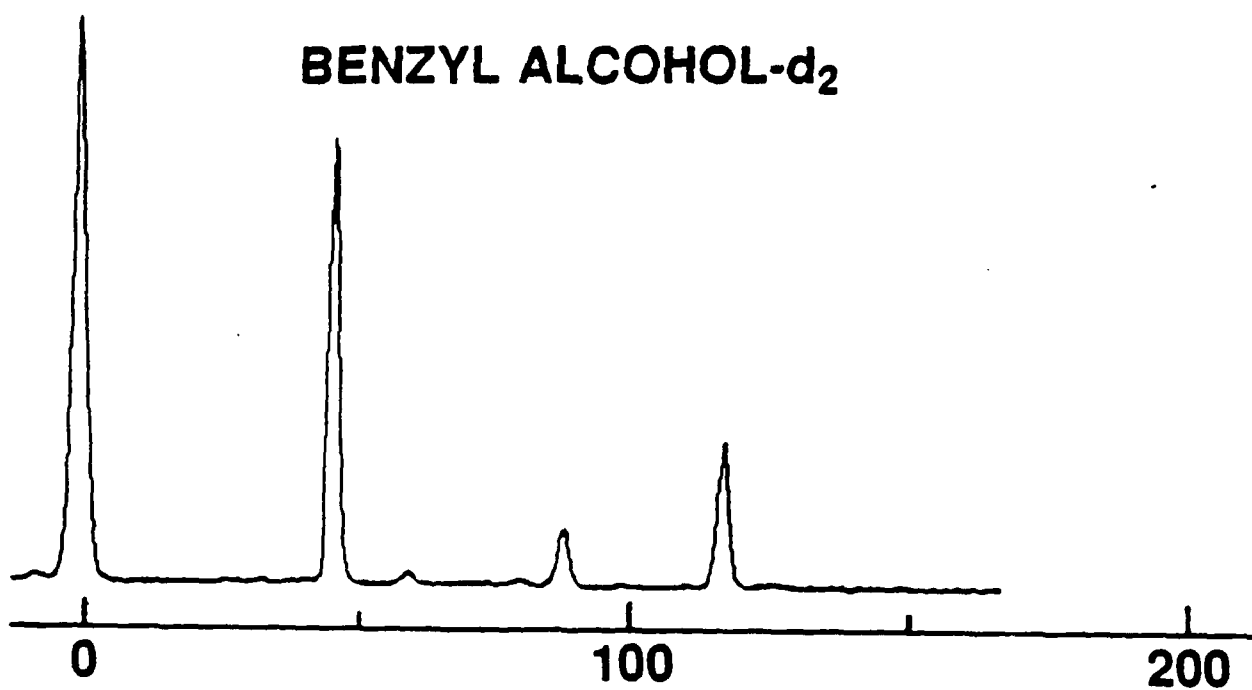
| ν a | $\nu-w(0_0^0)$ (cm ⁻¹) | Assignment |
|---------|------------------------------------|------------|
| A | 0 (37331.6) | 0_0^0 |
| B | +8.8 | T_0^2 |
| C | 34.9 | T_0^1 |
| D | 108.1 | $16b_0^1$ |

a. A through D are the notation for the observed vibronic features in Fig. 4.

(a) **A** **BENZYL ALCOHOL-h₂**

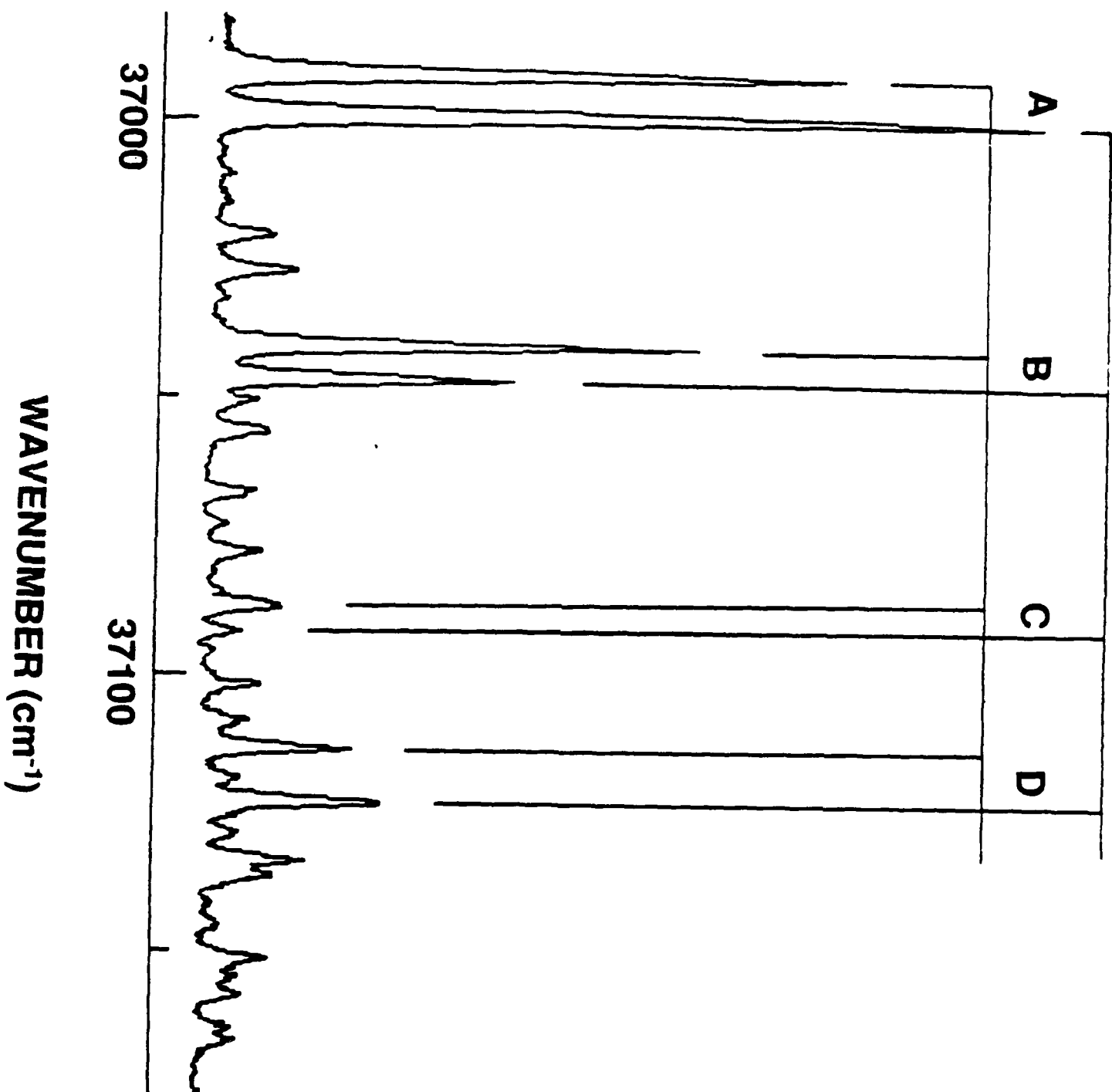


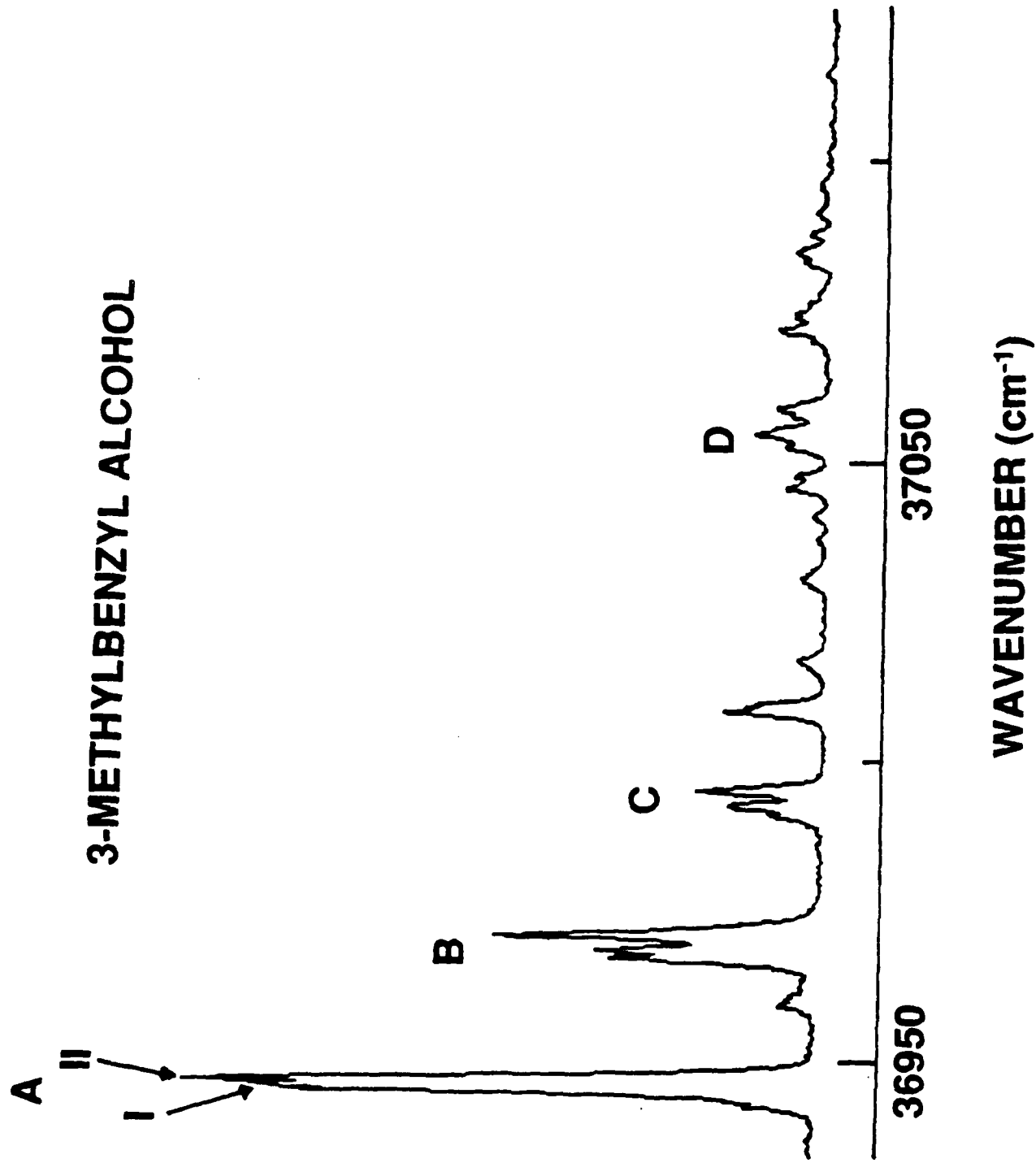
(b) **BENZYL ALCOHOL-d₂**



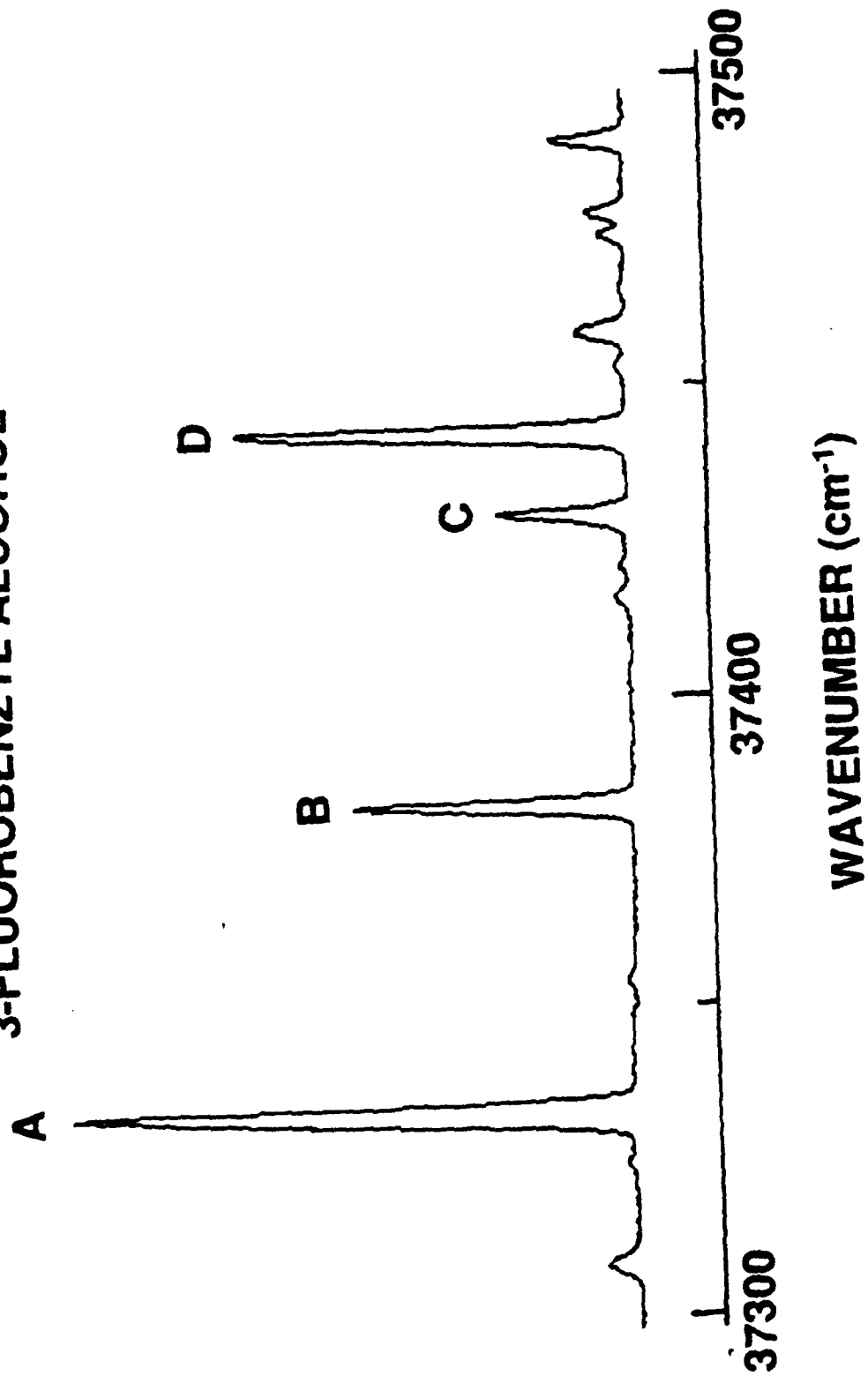
ENERGY (cm⁻¹)

4-ETHYLBENZYL ALCOHOL

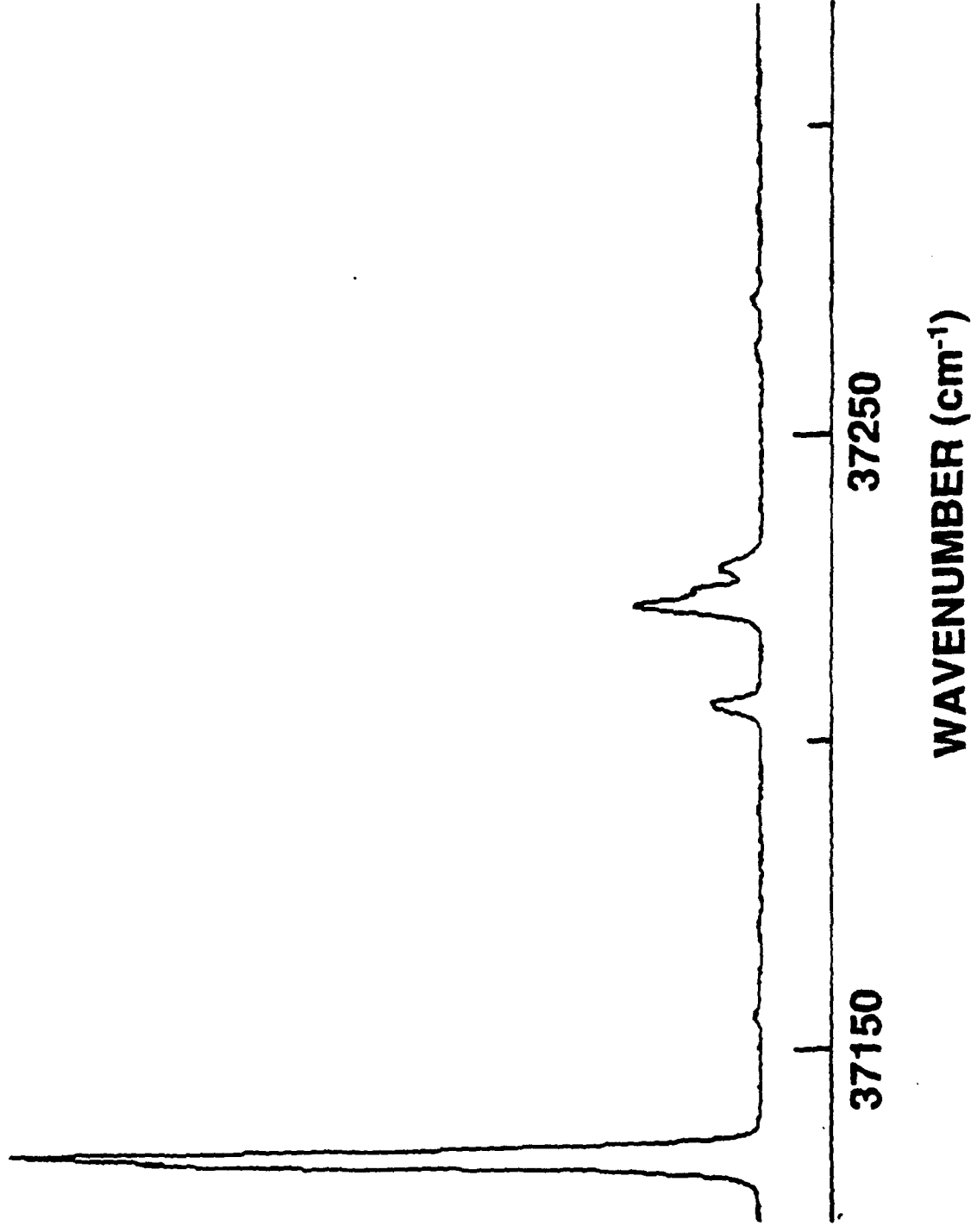




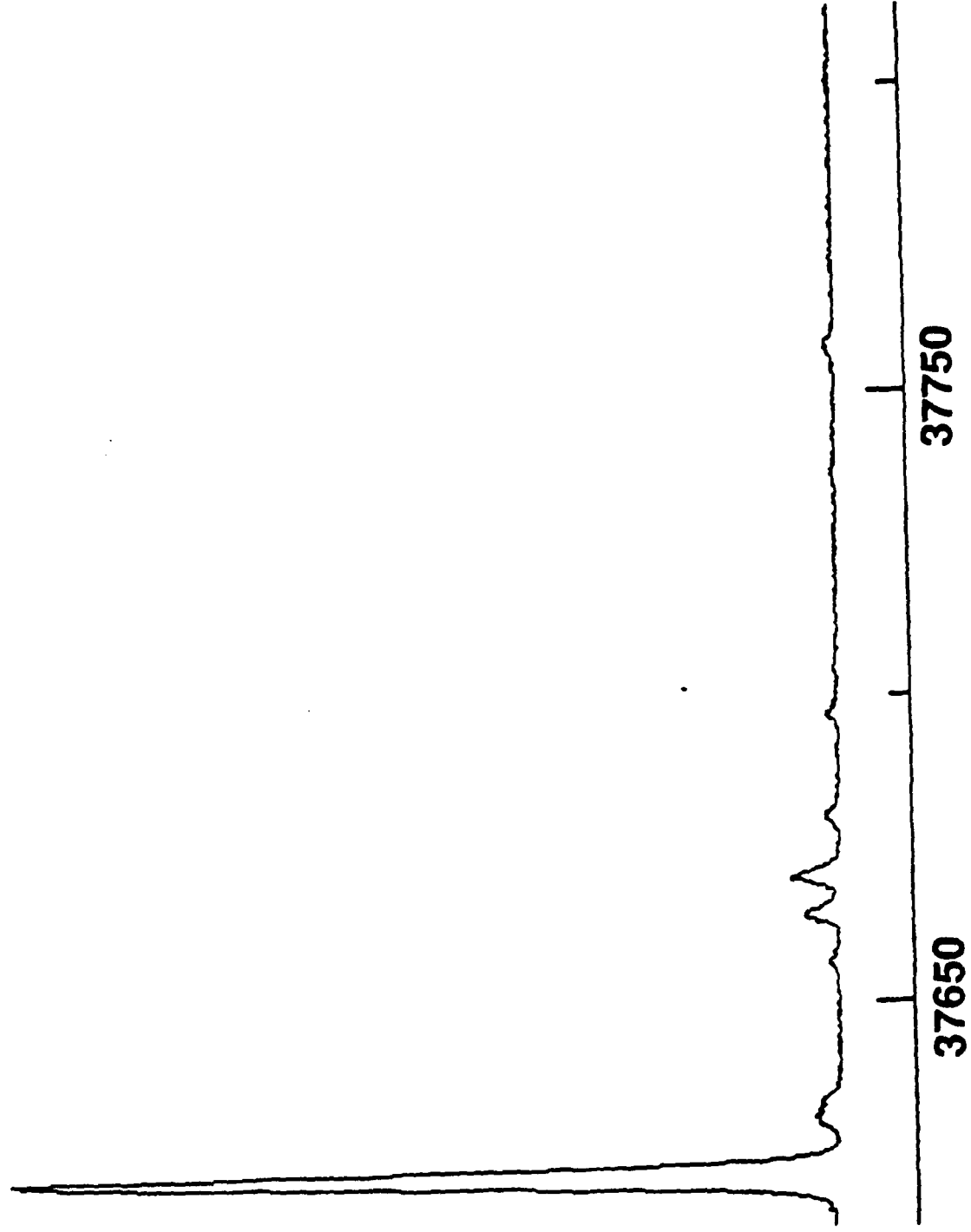
3-FLUOROBENZYL ALCOHOL



2-METHYLBENZYL ALCOHOL

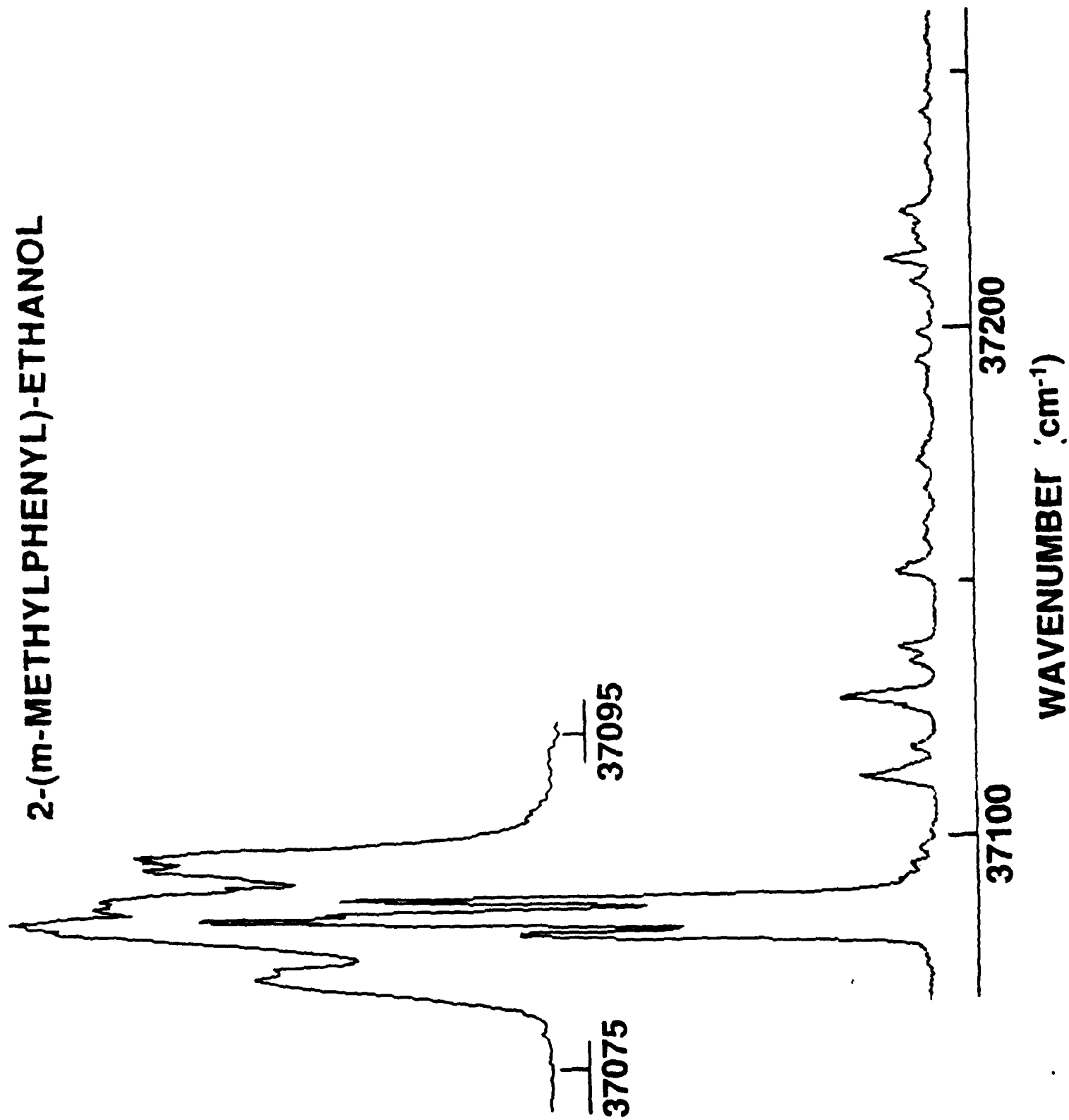


2-PHENETHYL ALCOHOL

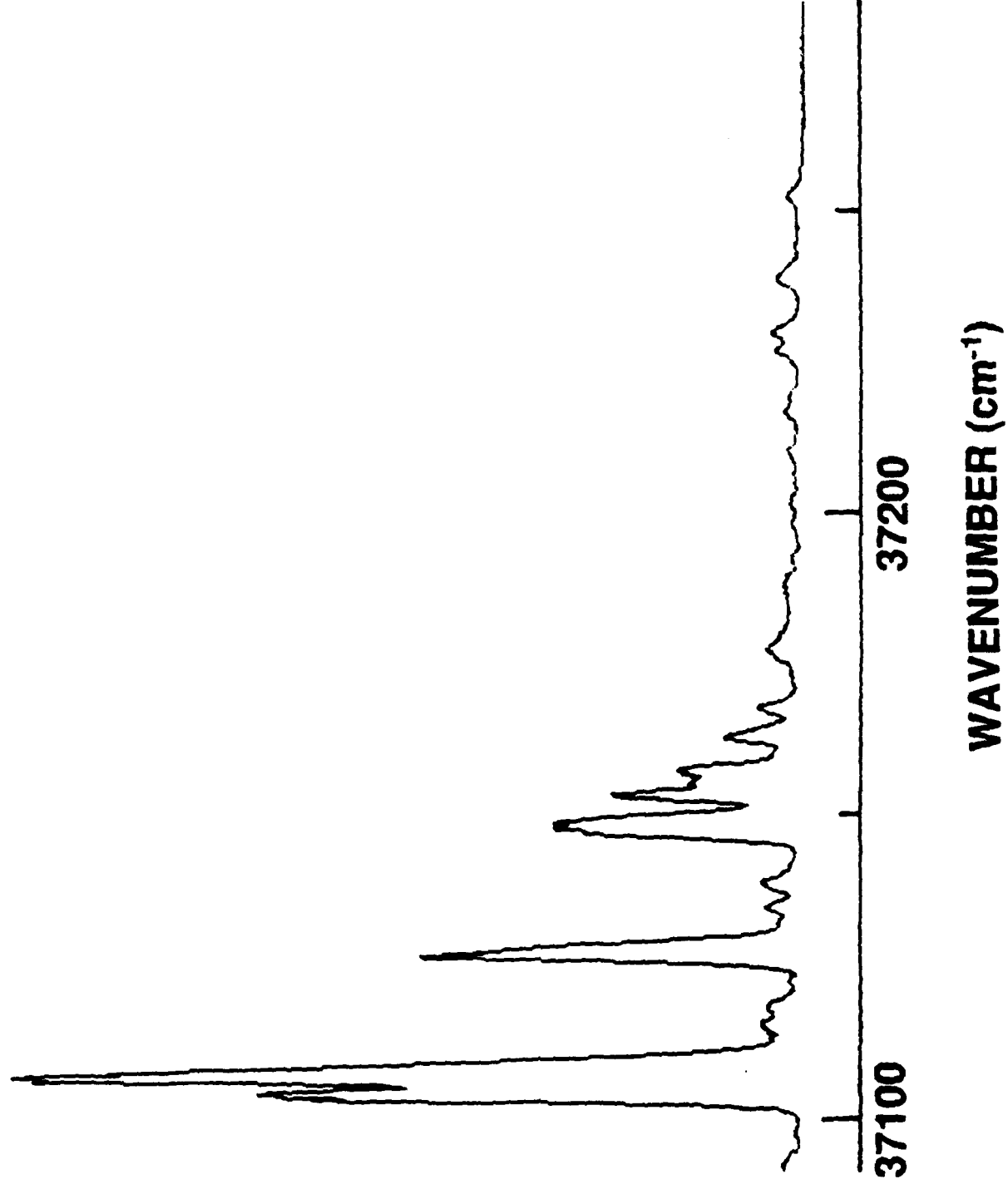


WAVENUMBER (cm⁻¹)

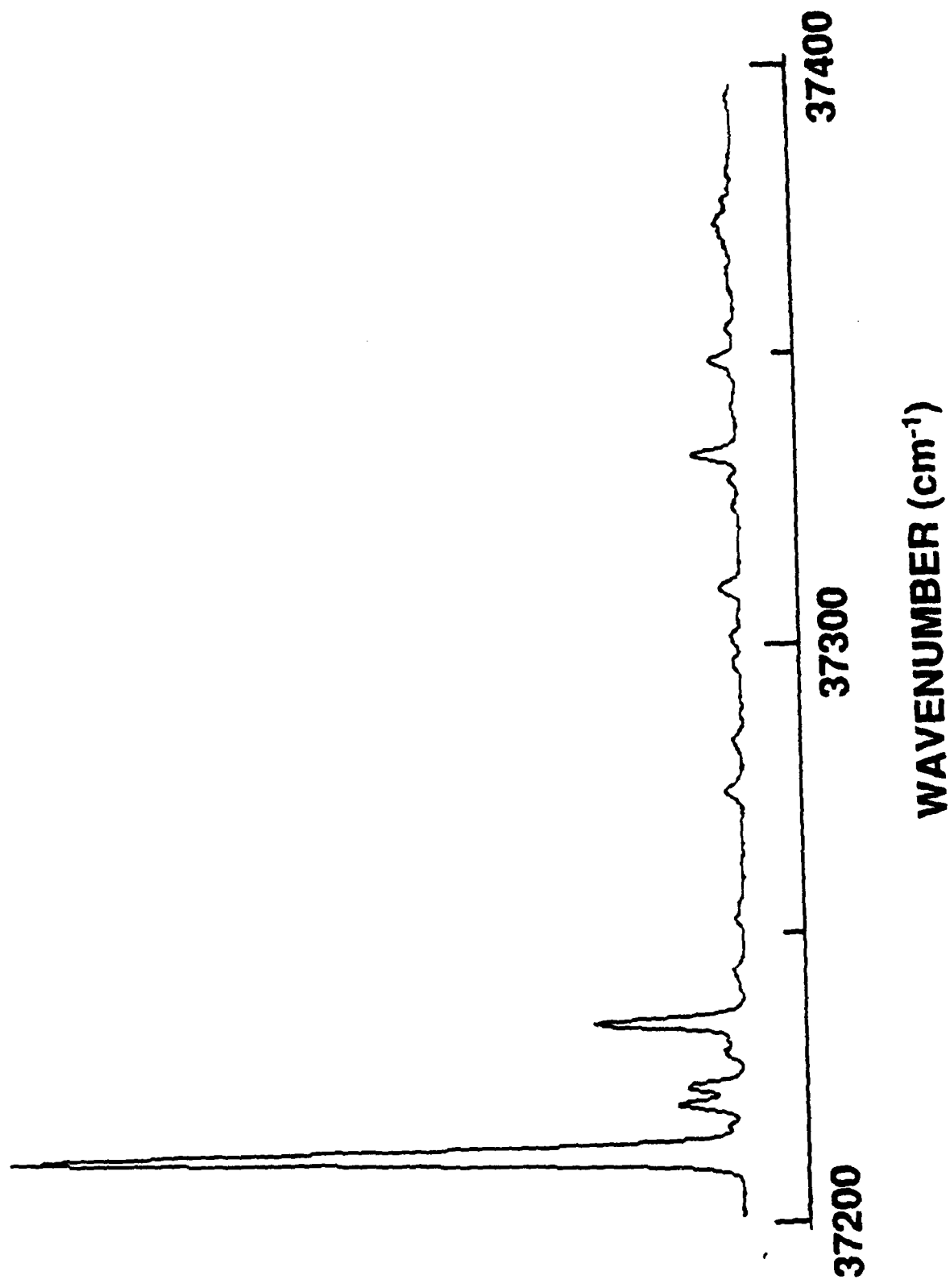
2-(m-METHYLPHENYL)-ETHANOL



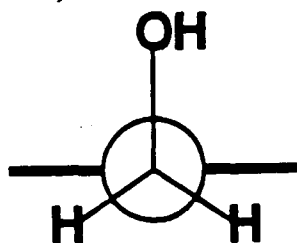
2-(m-METHYL-d₃-PHENYL)-ETHANOL



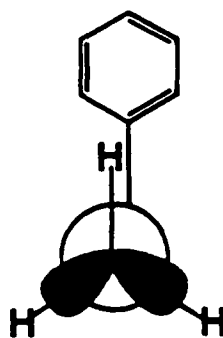
2-(o-METHYLPHENYL)-ETHANOL



(a)

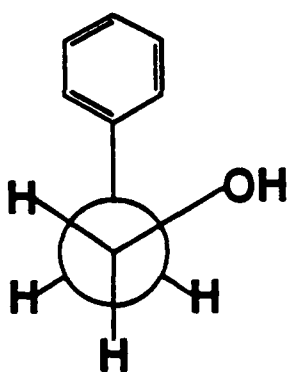


$$\tau(\text{C}_{\text{ortho}}-\text{C}_{\text{ipso}}-\text{C}_{\alpha}-\text{O})=90^{\circ}$$

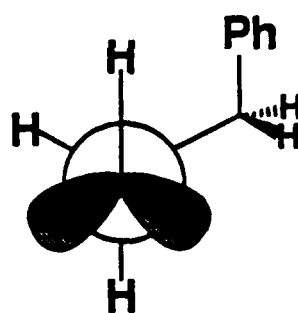


$$\tau(\text{C}_{\text{ipso}}-\text{C}_{\alpha}-\text{O}-\text{H})=0^{\circ}$$

(b)

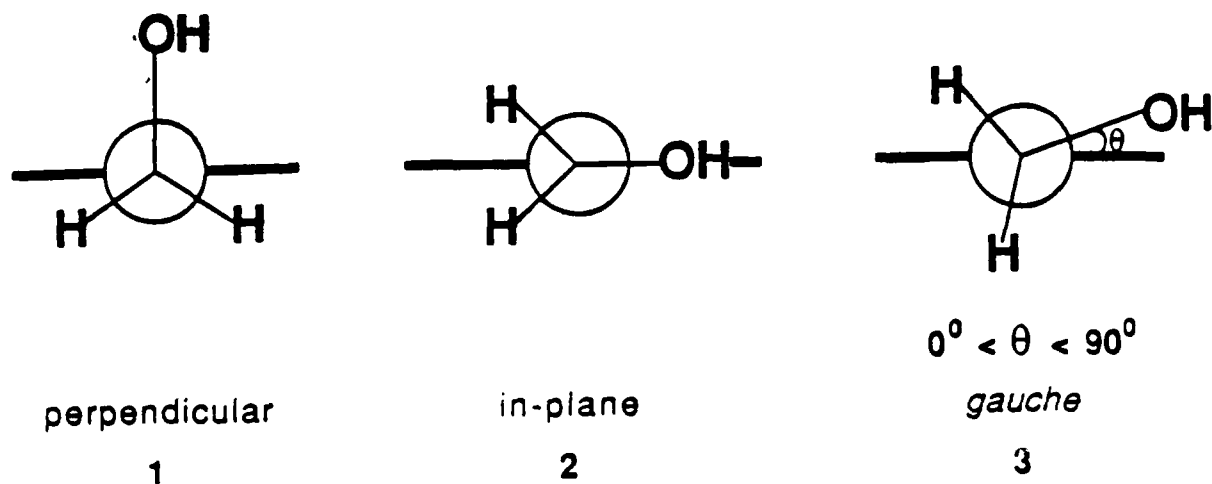


$$\tau(\text{C}_{\text{ipso}}-\text{C}_{\alpha}-\text{C}_{\beta}-\text{O})=60^{\circ}$$

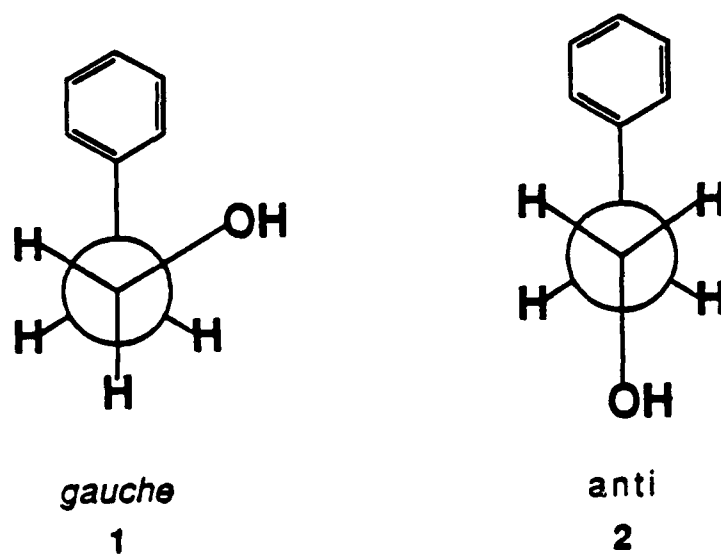


$$\tau(\text{C}_{\alpha}-\text{C}_{\beta}-\text{O}-\text{H})=60^{\circ}$$

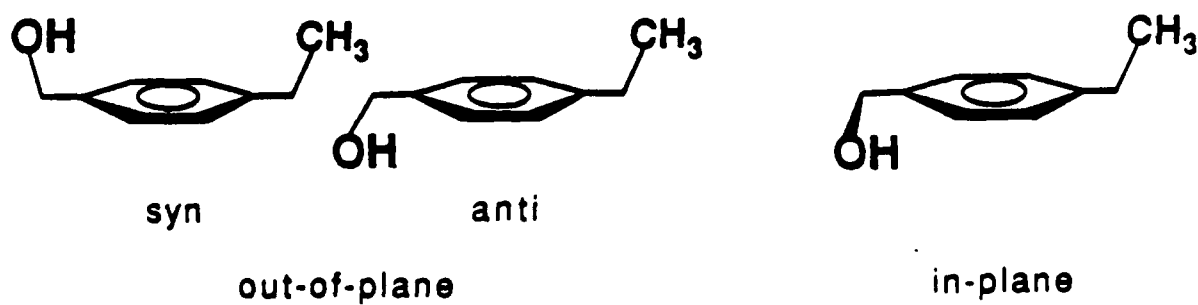
Scheme I



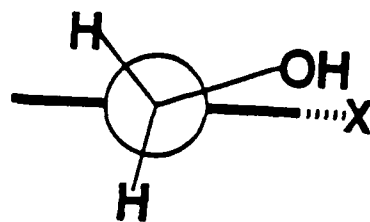
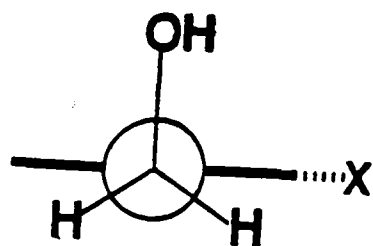
Scheme II



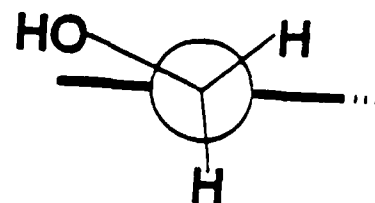
Scheme III



Scheme IV



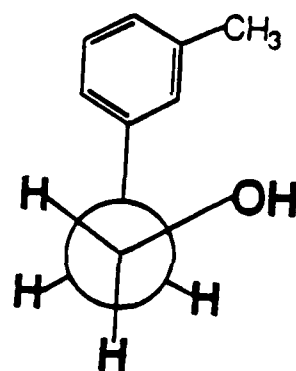
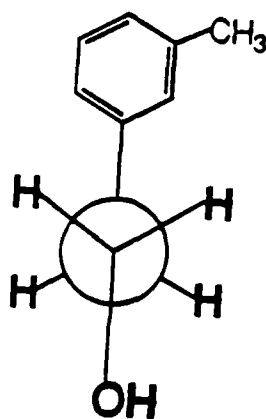
syn



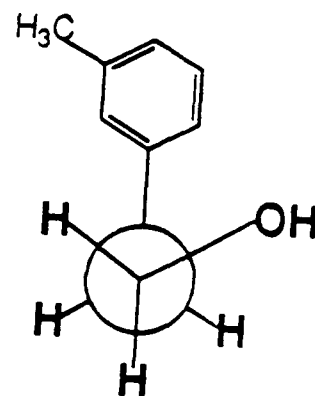
anti

perpendicular

Scheme V



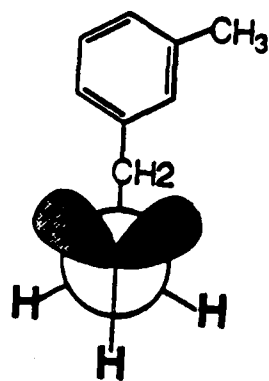
syn



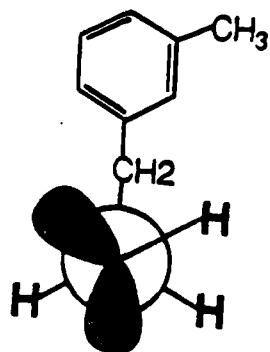
anti

anti-staggered

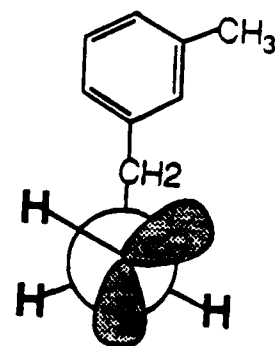
Scheme VI



anti-staggered



syn-gauche



anti-gauche

DL/1113/89/1

TECHNICAL REPORT DISTRIBUTION LIST, GENERAL

| | <u>No. Copies</u> | | <u>No. Copies</u> |
|--|------------------------------------|--|-----------------------|
| Office of Naval Research Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000 | 3 | Dr. Ronald L. Atkins Chemistry Division (Code 385) Naval Weapons Center China Lake, CA 93555-6001 | 1 |
| Commanding Officer Naval Weapons Support Center Attn: Dr. Bernard E. Douda Crane, IN 47522-5050 | 1 | Chief of Naval Research Special Assistant for Marine Corps Matters Code OOMC 800 North Quincy Street Arlington, VA 22217-5000 | 1 |
| Dr. Richard W. Drisko Naval Civil Engineering Laboratory Code L52 Port Hueneme, California 93043 | 1 | Dr. Bernadette Eichinger Naval Ship Systems Engineering Station Code 053 Philadelphia Naval Base Philadelphia, PA 19112 | 1 |
| Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314 | 2 <u>high</u> <u>quality</u> | | |
| David Taylor Research Center Dr. Eugene C. Fischer Annapolis, MD 21402-5067 | 1 | Dr. Sachio Yamamoto Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000 | 1 |
| Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000 | 1 | David Taylor Research Center Dr. Harold H. Singerman Annapolis, MD 21402-5067 ATTN: Code 283 | 1 |